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Studies on the Camphor Series, XII. Catalytic Activity of Various Reduced Coppers on l-Menthol.

By

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(Received April 11, 1927)

In the previous article, Prof. S. Komatsu and M. Kurata[1] have noted that the variability in the catalytic behaviour of reduced copper toward l-menthol, is affected greatly by the process by which the catalyst is prepared from various copper salts. Recently, Dr. B. Masumoto[2] in our laboratory, has observed on the catalytic action of various forms of copper oxide on pinene hydrochloride that the formation and physical nature of camphene depend on the modes of preparation of these catalysts, and these facts led the writer to undertake the present research.

The catalysts used in the experiment were prepared from the oxides of copper by reduction with hydrogen at 200°, and these were obtained by the writer according to the directions given by Dr. B. Masumoto in his paper above mentioned.

The density, and the bulk gravity (the volume occupied by one gram of the material when shaken down in a stoppered tube), of the catalysts were measured, and these properties seem to have some analogy to the colour of reduced metals, as will be seen in Table I. In Table I, Cu I was obtained from copper hydroxide gel from copper nitrate and a

1 These Memoirs, A, **8**, 147 (1925).
2 Ibid., **10**, 175 (1927).

potassium hydroxide solution and heated at 250°–300°. Cu II was prepared from crystalline copper hydroxide obtained from basic copper nitrate. Cu III was obtained from amorphous copper hydroxide. Cu IV, from basic copper nitrate of a grey colour by ignition at 250°–300°. Cu V, from black copper oxide which was formed from copper nitrate and 20 % ammonia water. Cu VI, from the copper oxide obtained from basic copper nitrate and excess of ammonia water and ignited at 250°. Cu VII, from the copper oxide resulting from the ignition of copper nitrate at 250°–300°.

Table I.

	d_4^{11}	bulk gravity	colour
Cu I. Colloidal gel	5.8135	0.1720	dull red
Cu II. Crystalline	4.9504	0.2020	brownish black
Cu III. Amorphous	4.2832	0.2335	black
Cu IV.	5.4193	0.1845	dull red
Cu V.	5.2543	0.1903	brown
Cu VI.	5.3630	0.1862	reddish brown
Cu VII. Ignited	5.7683	0.1774	vermilion

In the experiment, 5 grm. of every copper oxide were reduced at 200° with hydrogen as usual, and menthol, M. p. 41°, $[\alpha]_D=-49°\cdot0$, was passed with almost equal rate over catalysts heated to 250°. By the reaction, hydrogen gas, water and oily substance were noticed to formed. However, the quantity of these reaction products and the nature of the constituents of oily substance are largely depend upon the kind of the catalyst, though the conditions under which the reaction was proceeded were kept in a similar manner.

The amount of hydrogen gas evolved by the reaction was measured, from time to time, for every five minutes, which was plotted against time and the results are shown in Fig. 1, 2, 3, 4, 5.

The oily substance, formed by the reaction with some water, was separated from the water layer, its physical constants measured, and then fractionated by distillation in a Witmer flask into the following three parts;

1st. fraction to 190°
2nd. ,, 190°–210°
3rd. ,, above 210°

The first fraction was distilled on metallic sodium and the fraction, B. p. 164°–167°, was designated as menthene after confirmation of its

physical constants. The second fraction, B. p. 190°–210°, was noticed in one case, on standing for a while, to be solidified in a mass, and in other cases remained in a liquid state, and in the former case the fraction was confirmed to consist mostly of unchanged menthol from its physical nature, while in its oily state it was composed of a mixture of menthol and menthone. The proportion of the two components in the oily mixture was estimated by means of phthalic anhydride and semicarbazid, transforming the alcohol into a phthalic acid ester and the ketone into its semicarbazone. The third fraction which boils above 210°, was assigned

Fig. 1. Cu VI.

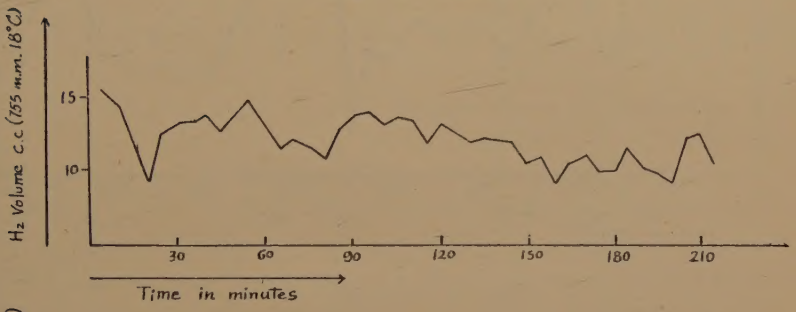


Fig. 2. Cu V.

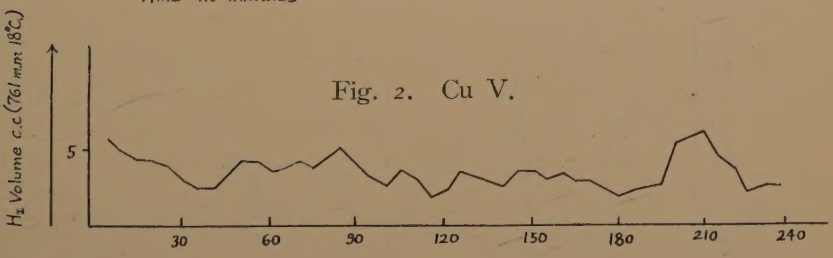


Fig. 3. Cu VII.

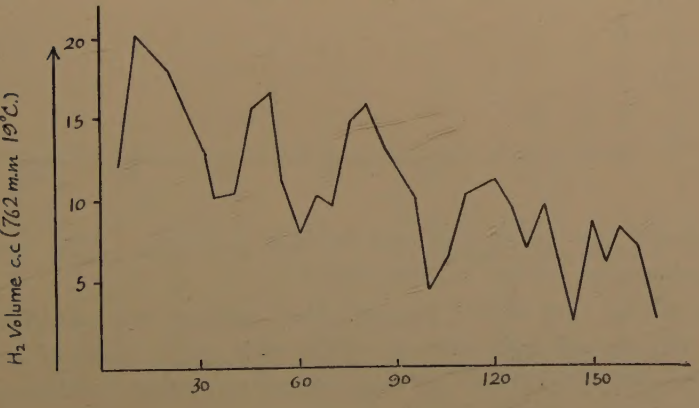


Fig. 4. Cu II.

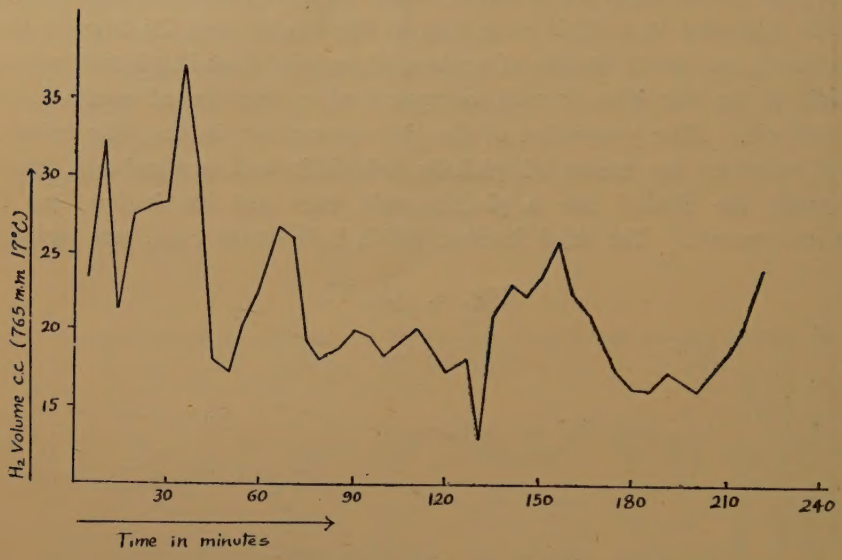
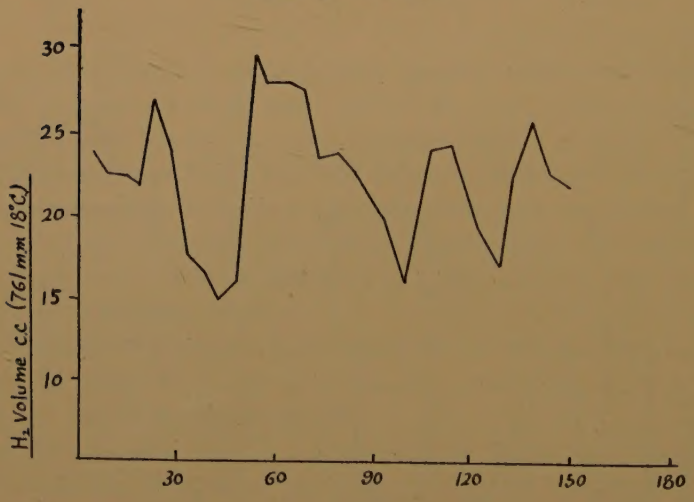


Fig. 5. Cu III.



to be thymol from its physical and chemical properties. The results of the experiment are shown in Table II.

As will be seen in that Figures, when menthol was passed on Cu I and Cu IV, no gas was evolved; while with other kinds of copper a certain amount of hydrogen gas was noticed to evolved, and its quantity

Table II.

Catalyst	Cu I	Cu VII	Cu IV	Cu VI	Cu V	Cu II	Cu III
Density of CuO	5·814	5·768	5·419	5·363	5·254	4·950	4·283
Colour of Reduced Cu	dull red	vermilion	dull red	reddish brown	brown	brownish black	black
Grm. Passed per hour	6·7	6·9	6·9	5·2	4·8	7·7	7·5
Menthol (grm.)	20.	20.	8·5	20.	20.	30.	20.
Reaction Product (grm.)	17.	19.	7·0	17.	19.	29.	19.
Reaction product $[\alpha]_D$	−21°·2	+12°·1	−47°·0	+3°·0	−33°·3	−4°·9	−2·°3
Reaction product n_D^{25}	1·4478	1·4488	—	1·4456	1·4479	1·4520	1·4673
Reaction product d_4^{25}	0·8505	0·8913	—	0·8899	0·8913	0·9029	0·8785
Production of Water	+	—	—	—	—	—	+
Fraction I (Menthene) B.p.	165°–170°	—	—	180°–200°	160°–180°	189°–200°	160°–190°
Fraction I (Menthene) $[\alpha]_D$	+7°·1	—	—	+2°·0	+3°·0	+7°·0	+2°·43
Fraction I (Menthene) n_D^{25}	1·4427	—	—	1·4463	—	1·4460	1·4493
Fraction I (Menthene) d_4^{25}	0·8113	—	—	—	—	—	0·8234
Fraction I (Menthene) yield %	49·	—	—	6·0	2·6	2·0	46.
Fraction II Menthone B.p.	—	202° 209°	—	202°–208°	202°–206°	204°–208°	—
Fraction II Menthone $[\alpha]_D$	—	+12°·2	—	+4°·4	+14°·1	−4°·9	—
Fraction II Menthone n_D^{25}	—	1·4468	—	1·4474	—	1·4487	—
Fraction II Menthone d_4^{25}	—	0·8913	—	0·8925	—	0·8944	—
Fraction II Menthone yield %	—	92·6	—	77·	—	80·	—
Fraction II Menthone M.p. of Semicarbazone		173°–176°	—	—	169°–172°	—	—
Fraction II Menthol M.p.	41°–42°	—	43°·	—	40°–42°	—	—
Fraction II Menthol $[\alpha]_D$	−50°·2	—	−48°·1	—	−50°·2	—	- -
Fraction II Menthol yield %	45·8	—	95·	—	31·	—	- -
Fraction II Menthol M.p. of acid phthalate		—	—	—	104°–110°	—	25·
Fraction III (Thymol) M.p.	—	—	—	—	—	43°–44°	100°–108°
Fraction III (Thymol) yield %	—	—	—	—	—	2·0	14·

depending largely upon the nature of catalyst, with Cu V and Cu VI, the evolution of the gas is constant during the experiment, while with Cu VII, it shows a gradual decrease with the progress of the reaction. With Cu II and Cu III, the curves for hydrogen gas show a zigzag form which indicates that the reaction in presence of the catalysts will be more complicated than in the other cases, and such an idea of the reaction will be foretold on the appearance of water in the reaction product.

In the case of Cu III, some quantity of water was noticed to form by the reaction, because of this water the reaction product was emulsified.

The formation of water by the reaction was also observed with Cu I. The reaction product, however, in this case seem to differ in nature from those of Cu III, since no hydrogen gas was noticed to evolve in the former as stated above. With Cu I and Cu IV, there is a similarity in the fact that no hydrogen gas is formed in the reaction; while they differ with regard to the formation of water. The behaviour of Cu IV, Cu VII, Cu VI, Cu II and Cu V toward menthol seems to be similar in the fact that no water is formed, but there is a difference in the formation of hydrogen gas.

Such a difference in the formation of water and hydrogen gas by the reaction with various catalysts was also noticed in the chemical nature of the oily reaction products in some measure; the products which were formed in presence of Cu I and Cu III, are alike in the quantity of menthene, but differ in the occurrence of thymol, and these facts were manifested in the formation of hydrogen gas and water. In other words, with Cu I, the dehydration of menthol takes a prominent part in the reaction; while with Cu III, the dehydration and the oxidation of menthol take place simultaneously, and the former catalyst serves as a dehydrating agent, and the latter as dehydrating and oxidizing agent. Cu II behaves toward menthol as a dehydrating and oxidizing agent just like Cu III, the oxidizing action of the former, however, is different in details from the latter, forming menthone as a principal reaction product.

The catalytic action of Cu VII, Cu VI and Cu V is similar to Cu II in producing menthone, but the rotatory power of menthone formed by the action of the three former catalysts is different from that formed by the last one. The catalytic activities of these reduced coppers, therefore, differ greatly from each other in detail though they are practically similar in the main points of reaction. Analogous phenomena may be noticed in the menthene fraction with these catalysts.

In summary, Cu VII, as noticed already by Sabatier on the catalytic action of reduced copper, acts on menthol as an oxidizing catalyst forming

menthone, and other catalysts except Cu I, act to promote the oxidation of menthol, but the activities of these catalysts differ from each other, especially those of Cu II and Cu III, possessing the faculty to remove the hydrogen atoms of the polymethylene ring, consequently Cu VII is the most convenient catalyst for making menthone from menthol, and Cu VI, Cu V and Cu II may be used as catalysts for this purpose, and Cu III is in like manner a good catalyst for the preparation of thymol.

Cu I acts on menthol to dehydrate it, with the formation of menthene, which is similar in catalytic activity to alumina or thoria; and Cu III, as will be seen in the results shown in Table II acts as a dehydrating catalyst.

The reduced coppers will be divided from the stand-points of catalytic activity toward menthol, into two classes, the first group which acts to promote the oxidizing action of menthol, as we noticed with reduced nickel, to which Cu VII belongs; and the second group acts on menthol to promote dehydration, and Cu I belongs to this group. Other reduced coppers have both of these catalytic actions, though the activity of these actions differs according to the processes by which these catalysts are prepared from nitrate.

The activity and nature of the catalytic actions of these catalysts are independent of their specific gravity but seem to depend upon the mode of the formation of the catalysts, and their nature may be ascribed to the special features of the catalysts.

This research was carried out at the suggestion and under the direction of Prof. S. Komatsu, to whom the writer wishes to express his sincere thanks.

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Lengths of Enhanced Lines of Metals excited in Various Media and Lines of Constant Wave Number Differences among Enhanced Lines of Bismuth and Lead.

By

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Abstract.

Lengths of enhanced lines of metals excited in various media: In the present experiment the spark spectra of Cu, Zn, Al, Pb, Bi, Cr, Mn and Ni produced in atmospheres of hydrogen, water-vapor, nitrogen, oxygen and halogen were photographed, and the appearance of the enhanced lines excited in these media was examined. It was found that the spark and super spark lines produced in the above mentioned media the lines obtained by the spark in hydrogen were longest, and when that medium was replaced by water-vapor, nitrogen, oxygen and halogen respectively, their lengths were shortened in that order.

Lines having oonstant wave number differences: Lines having constant wave number differences were found among enhanced lines of lead and bismuth.

Spark lines of elments have already been classified by many investigators. Kimura and Nakamura[1] recently introduced a very convenient and simple method of classifying such lines. Their method is simply to compare the lengths of lines in the spectrum of condensed discharge. The results thus obtained in the cases of silicon and of aluminium are in harmony with those obtained by Paschen and Fowler. In the experiment of Kimura and Nakamura, the condensed discharge was sent between metal electrodes placed in air. In the present experiment, however, the sparks were produced in various media namely, hydrogen, water-vapor, nitrogen,

1 Jap. J. phys., **3**, 197 (1924).

oxygen, chlorine. etc., and the change thus called forth in the appearance of enhanced lines was examined. As the electrodes, the following metals were used: Cu, Zn, Al, Pb, Bi, Cr, Mn and Ni.

Apparatus.

In the present experiment two discharged lamps were used, of the form shown in Figs. 1 and 2. The lamp shown in Fig. 1 was made of a glass tube having an internal diameter of about 3 cm., and a length of 15 cm. Both ends of the tube were closed with rubber-plugs containing electrodes placed in glass tubes. The upper plug had another glass tube B. The space surrounding the metal electrode in the glass tube was packed with Indian rubber. The length of the spark gap G was fixed at 6 mm. The lamp has 2 side tubes S and W, the internal diameter of the latter tube, which has a quartz window at W, being 2.2 cm. and its length 4 cm.. The lamp shown in Fig. 2 was made of

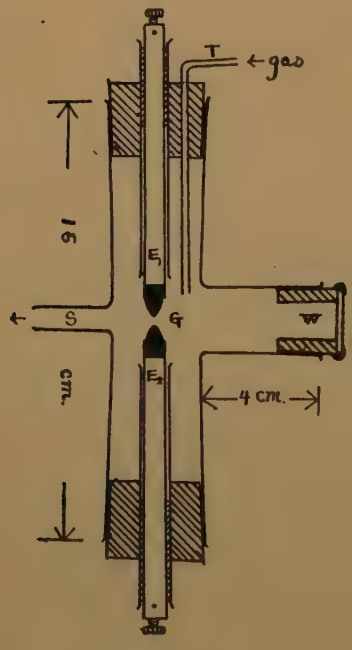

Fig. 1.

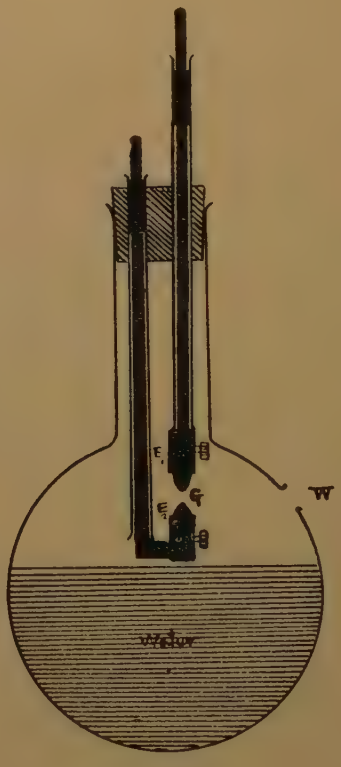

Fig. 2.

a one litre flask having an opening at W. The electrodes were placed

in the flask through the rubber-plug, the ends of the electrodes being cut down into the form of truncated cones. A pair of these lamps were placed facing each other as shown in Fig. 3, (b), the distance between S_1 and S_2 being about 30 cm. These two sparks were connected in series with a variable self-induction L, auxiliary spark gap G and a variable condenser C, the latter being charged by a transformer of 1 K. W. capacity giving 30000 V. in the secondary. The capacity of the condenser was varied from about 0·001 to 0·005 microfarads, and the discharge current did not exceed 0·3 amperes.

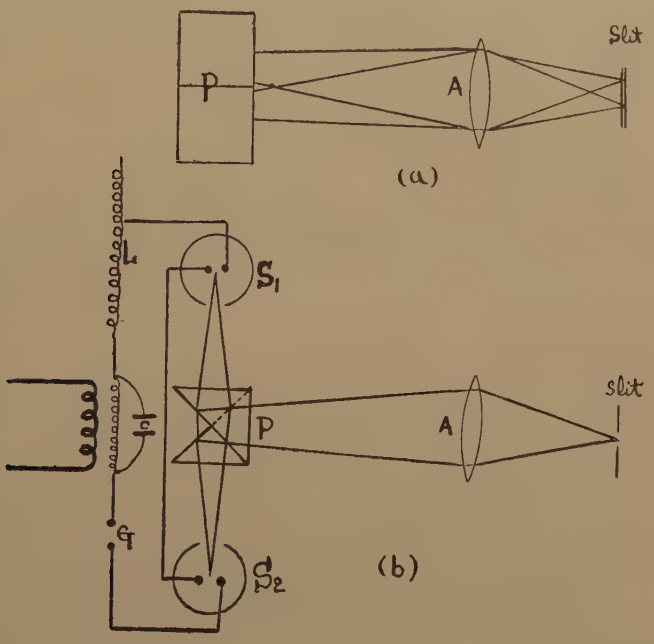

Fig. 3.

A Hilger quartz spectrograph of size E_6 and a Fuess quartz instrument of size B and a prism spectrograph with a large direct vision prism provided with a camera having a photographic lens of 60 cm. focus were used to photograph these spectra.

In the case of the discharge in the media of hydrogen, nitrogen, oxygen and chlorine, two lamps of the form 1 were used, the gas being introduced into one of the lamps through the tube B. Hydrogen was prepared by the action of dilute sulphuric acid on zinc chlorine by the action of hydochloric acid on manganese dioxide, and nitrogen by heating a mixture of ammonium nitrite and sodium sulphite. Oxygen was obtained

from a cylinder containing the compressed gas. In the case of the discharge in watervapor, sparks were produced in lamps of the form shown in Fig. 2, the water in one of them being boiled. Two right-angle quartz prisms P and a quartz-fluorite achromatic combination A were so adjusted that the images of the two sparks S_1 and S_2 were formed one above the other on the slit of the spectrograph, as shown in Fig. 3, (a) and (b).

The photographs were taken on Ilford rapid process panchromatic plates and also on Ilford process plates sensitized with paraffine oil for extreme ultra violet. Thus spectra of lights emitted from sparks in air and in a gaseous medium were photographed at the same time on one plate, and the appearances of lines were carefully examined.

Results.

(1) Nitrogen and oxygen.

In air and nitrogen the modes of the appearance of lines in spark spectra of seven elements mentioned above did not show any marked difference. In oxygen, however, certain lines showed a greater broadening than in air. The photographs of lead spectrum taken in oxygen and nitrogen are represented in Figs. 4, b and c, Pl. XII.

(2) Chlorine Bromine and Iodine.

When the sparks were sent between electrodes of zinc, lead and bismuth, placed in chlorine gas their chlorides were soon produced, and the fumes soon obscured the lights. To prevent this, the sparks were intermittently sent and the chlorides deposited on the quartz window were frequently cleared off. The spectra of these lights were markedly different from those in air. These are shown in Figs. 4, a and 5, a, Pl. XII, 6, a and 7, a, Pl. XIII. In the atmosphere of chlorine spark lines increased in intensity while the lengths of super spark lines decreased, and some super spark lines and super-super spark lines disappeared entirely in the spectra. The light in the ultraviolet region extending from λ 3800 to 2800 was wholly absorbed by chlorine. In the case of copper, zinc, aluminium, lead and bismuth, certain lines were found to be broadened out considerably.

In bromine and iodine atmospheres, the lights were strongly absorbed by these gases, so that only a part of the spectra was examined. The result, however, was similar to that of chlorine.

(3) Hydrogen.

In the hydrogen atmosphere the lights emitted from the sparks between various electrodes became faint giving a deep red colour. To photograph these spectra, an exposure six times longer than that given

with the air spark was required to get nearly equal photographic intensities of the spark lines. In hydrogen, spark lines appeared long, as if they were arc lines in an air spark, and super spark lines short, showing an appearance of spark lines in air spark, and super-super spark lines shortest, but their appearance was like that of super spark lines in air spark, the intensity of super-super spark lines being much enhanced as compared with that of the spark lines. Such spectra of lead and bismuth are represented in Fig. 4,f, Fig. 5, c, Pl. XII, Fig. 6, d and Fig. 7, d, Pl. XIII.

(4) Water-Vapor.

In water-vapor the spark lines looked almost the same as corresponding lines in air, while super spark and super-super spark lines were longer and more intense than those of air spark. The characteristic differences in appearance between the lines of these three types were clearly seen in the spark spectra produced in water-vapor. These are shown in Figs. 4, e; 5, b, Pl. XII, Figs. 6, b; 7, b, Pl. XIII. Certain lines which were not classified by Kimura and Nakamura were observed in these spectra. Their wave-lengths were taken from Kayser's Handbuch and they were classified into spark and super spark, and super-super spark lines according to the method of Kimura and Nakamura as shown in Tables I, II, III and IV.

Table I, Cu.

CuIII			
5768	5635	5566	5486
5760	5618	5563	5439
5652	5608	5543	5268
5642	5574	5487	5204

Table II, Zn.

ZnIII			
5937	5207	3578	2308
5777	5190	2464	2253
5664	4416	2329	
5582	3661	2318	

Table III, Pb.

PbIII				PbIV
6380	4802	3736	2433	5143
5877	3950	3689	2299	
5164	3925	3089	2080	
5005	3854	2804	2060	

Table IV, Bi.

BiII	BiIII	BiIV		
4970	6053	6135	3159	2641
4908	6037	5542	3009	2582
4949	3846	5538	2973	2501
4748	3816	5527	2968	2479
4387	3394	3455	2822	2378
2396		3236	2757	2325
2246		3454	2746	2313
2187		2299	2733	2301
		3296	2730	2294
		3287	2684	2265
		3236	2677	2252

By passing sparks between metal electrodes placed in the seven media mentioned above, changes called forth in the appearance of enhanced lines were thus examined. In hydrogen, the lengths of super spark and super-super sqark lines were remarkably increased as compared with those of corresponding lines excited in air spark, while in water-vapor there was only a slight increase, and in nitrogen and oxygen, none. In halogen lengths and intensities of such lines were decreased and some of them disappeared entirely, while the intensitys of spark lines was enhanced considerably as compared with those excited in air spark. Thus among enhanced lines of higher orders produced in the above mentioned atmospheres, the lines obtained by the spark in hydrogen were longest, and when the medium was replaced by water-vapor, nitrogen, oxygen and

halogen the lengths were shortened in that order.

It may be interesting to notice that among the enhanced lines of lead and bismuth lines having constant wave number differeces were found and these are given in the following Tables V and VI.

Table V, Pb.

PbII.

Int	λ	ν vac.	Δ ν
9	5608·9	17828·8	8573·3
8	3786·5	26402·1	
5	2717·1	36793·1	8573·0
10	2203·6	45366·1	
10	4386·8	22788·8	759·5
10	4245·4	23548·3	
8	3017·6	33129·3	766·0
5	2949·4	33895·3	

PbIII.

Int.	λ	ν vac.	Δ ν
4	4571·5	21868·5	
4	3952·1	25295·8	3427·3
4	3176·5	31472·1	6176·3
4	3176·5	31472·1	
4	2864·4	34901·1	3429·0
2	2433·6	41078·9	6177·8
4	−4400·8	−22716·8	
4	−4801·9	−20819·3	1897·5
2	−5163·6	−19361·0	1458·3
3	4272·5	23398·9	
3	3925·2	25296·5	1897·6
3	3736·2	26757·6	1461·1

PbIV.

Int.	λ	ν vac.	ν
3	3242·8	30828·7	211·5
3	3220·7	31040·2	
3	3051·3	32763·4	211·8
2	3031·7	32975·2	
3	3927·7	25453·0	1894·5
3	3655·6	27347·5	
3	3279·2	30486·5	1896·9
3	3087·1	32383·4	

Table VI, Bi.

BiII.

Int.	λ	ν vac	Δ ν
10	5209·4	19190·7	
10	4259·8	23468·7	4278·0
10	3792·8	26358·3	2889·6
6	3111·4	32130·5	
3	2746·3	36401·9	4271·4
3	2544·4	39290·2	2888·3
7	6808·8	14682·8	
7	6599·7	15148·0	465·2
7	6497·7	15385·8	237·8
8	5270·5	18968·3	
8	5144·6	19432·5	464·2
6	5091·2	19636·6	204·1(?)
7	4391·4	22765·4	
10	4302·2	23237·4	472·0
10	4259·8	23468·7	231·3

Int.	λ	ν vac.	Δ λ
7	6059·0	16499·8	680·5
6	5819·0	17180·3	1159·2(?)
8	5456·2	18339·5	
8	5144·5	19432·8	680·3
4	4970·5	20113·1	1135·9(?)
10	4704·8	21249·0	
—	—	—	—
7	6590·8	15147·8	2332·6
8	5719·1	17480·4	
—	—	—	—
7	5655·7	17676·4	2332·9
6	4993·8	20019·3	
—	—	—	—
7	6497·6	15386·1	3804·2
10	5209·5	19190·3	
—	—	—	—
8	5144·6	19432·5	3805·1
10	4302·2	23237·4	

BiIII.

Int.	λ	ν vac.	Δ ν
5	5079·5	19681·5	1156·0
5	4797·7	20837·5	
3	3631·8	27526·7	1154·6
4	3485·6	28681·3	
4	3485·6	28681·3	96·6
4	3473·7	28777·9	
7	2855·7	35007·4	99·6
3	2847·6	55107·0	
2	4752·3	21037·0	2065·6
3	4327·3	23102·6	
3	3756·2	26615·1	2066·2
4	3485·6	28681·3	
5	5079·5	19681·5	7980·0
3	3614·1	27661·5	
3	3039·7	32888·4	7978·9
2	2446·2	40867·3	

BiIV.

Int.	λ	ν vac.	Δ ν
2	3287·3	30411·4	
			1227·0
2	3159·8	31638·4	
			2035·4
2	2968·8	33673·8	
3	3041·2	32872·2	
			1232·4
3	2931·3	34104·6	
			2035·4
2	2766·3	36140·0	
4	3473·9(IIIP)	28777·9	
			5489·2
2	2917·4	34267·1	
			2863·8
2	2693·1	37130·9	
2	3159·9	31637·4	
			5483·5
2	2693·1	37120·9	
			2868·6
2	2500·5	39989·5	
2	2773·1	36046·2	
			566·3
2	2730·5	36612·5	
			738·6
1	2676·5	37351·1	
2	3295·9	30332·0	
			561·5
2	3236·0	30893·5	
			744·9
2	3159·8	31638·4	

In conclusion, I wish to express my best thanks to Prof. M. Kimura, under whose guidance the present experiments were carried out.

Fig. 4. Pb.

Pb-Spark in

a Air,

b Chlorine, Air,

c Oxygen, Air,

d Nitrogen, Air, (Small Self-induction)

e Water-Vapor, Air,

f Water-Vapor, Air, Hydrogen. (6-Times-Exposure)

Fig. 5. Bi.

Bi-Spark in

a Air,

b Chlorine, Air,

c Water-Vapor, Air, Hydrogen. (6-Times-Exposure)

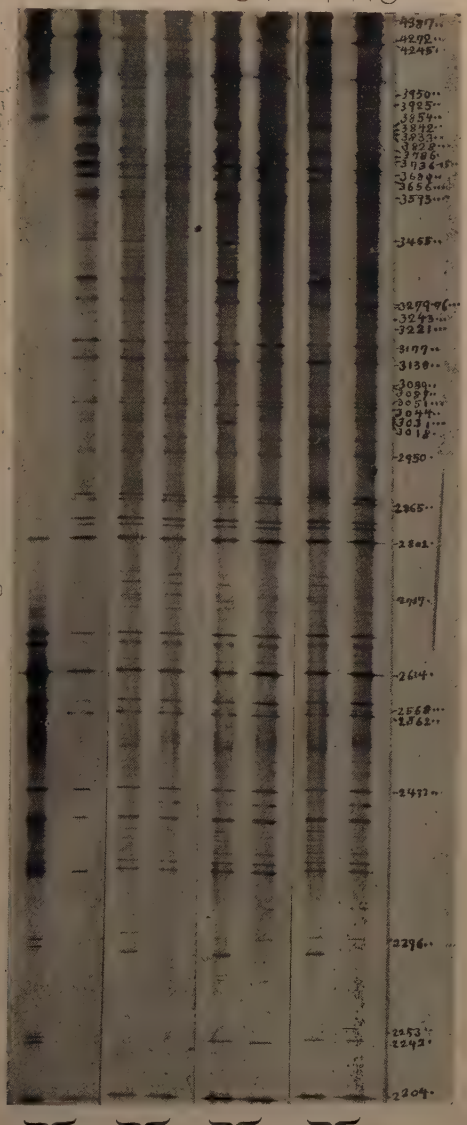

Fig. 6. Pb.

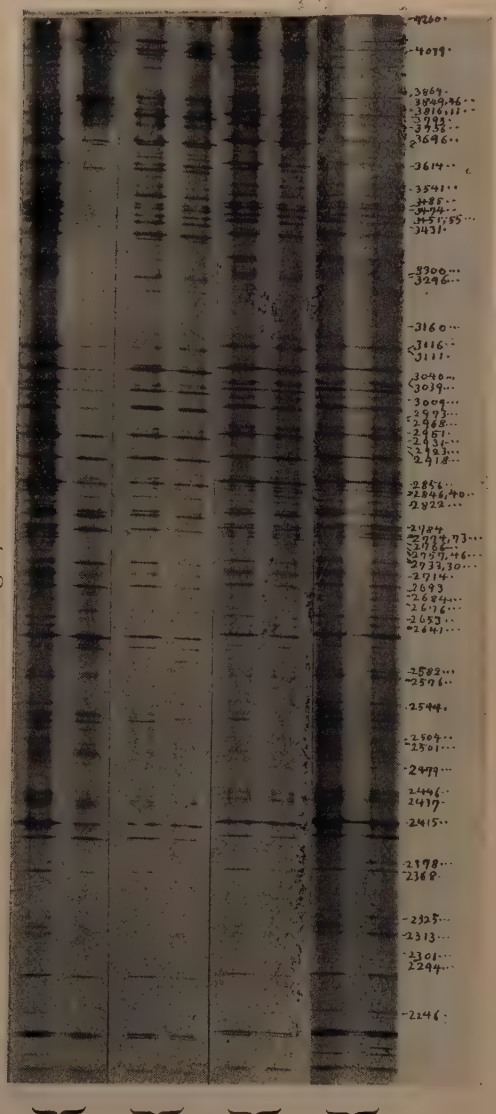

Fig. 7. Bi.

The Spectra of Metallic Arcs Started in Chlorine.

By

Michika Miyanishi.

(Received April 25, 1927)

Abstract.

In the foregoing experiment it was found that enhanced lines of tin were observed in its arc started in chlorine. In the present experiment, the object was to study the change called forth in the spectra of various metallic arcs and of metal flames from an electric furnace, when chlorine was introduced into the arc and furnace chambers. It was found that in chlorine arcs spark lines were enhanced and some super spark lines also made their appearance, and that in flames from the furnace, spark lines were also detected when chlorine was introduced. Thus the presence of chlorine in arcs and furnaces facilitates the emission of enhanced lines of metals.

In the foregoing experiment it was found that enhanced lines of tin were detected in light emitted from an arc in chlorine gas started between a tin electrode and a water-cooled copper one. In the present experiment, the spectra emitted from various metal arcs started in chlorine were examined.

Experimental method.

Arcs were started in the chlorine atmosphere in two different ways.

(1) In the case of metals having rather high melting points the arc was started between metal electrodes, but in the case of metals of low boiling-points the following method was used to obtain their arc :– A piece of a metal whose arc spectrum was to be studied was placed upon the flat surface of a water-cooled copper cylinder having a diameter of

5 cm. and a height of 2 cm. and this was used as the lower electrode. The upper electrode consisted of a water cooled copper tube provided with a copper cap. As is shown in Fig. 1, A, the lower electrode was fixed on the bottom of a glass-case of about two litres capacity, and this was connected to a negative terminal of 110-volts D. C. circuit, a choking coil being connected in the circuit. The air in the glass-case was displaced by chlorine and then the arc was started, the current being about 7 amperes.

(2) A small arc furnace having a base of $2{\cdot}5 \times 3$ cm^2. and a height of 3 cm. was constructed with bricks, and a window of about 1 square cm. was opened, as shown in Fig. B, so that it allowed flame to pass, but not the direct light from carbon electrodes. A small quantity of a

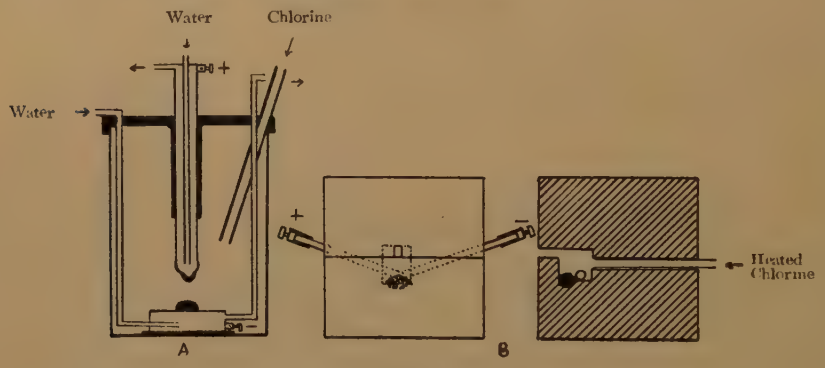

Fig. 1.

metal was placed in this furnace and this was heated by means of a 20 ampere arc in a chlorine atmosphere, the latter being introduced into the furnace through the tube shown in Fig. 1, B.

The lights emitted from the arc in the first apparatus and flame from the window in the second, were studied with a spectrograph having a large direct vision prism and a photographic lens of 60 cm. focus. The spectra thus photographed were compared with those obtained in an atmosphere of air instead of chlorine.

Results.

1 Sodium.

This metal in the molten state combines spontaneously with chlorine emitting light. By means of the arc apparatus (Fig. 1, A) mentioned above, an arc was started in air between metallic sodium and the water cooled copper electrode. Next, a similar experiment was carried out in an atmosphere of chlorine. In the latter case the light emitted was very

brilliant, giving a large quantity of sodium chloride-smoke. Examining the spectra of these lights it was found that in the former case combination lines λλ, 4918, 4914, 4633, 5629, etc. appeared feebly as shorter lines in the neighbourhood of the metallic sodium electrode while in the latter case they became enhanced as long lines. Besides this change unclassified feeble lines appeared at λλ, 4573, 4569, 4564, 4552, 4485, 4482, etc. To examine the nature of these lines, sparks were first passed between the electrodes consisting of this metal, placed in air and then sparks were passed in chlorine between the carbon electrodes, boiled in concentrated solution of NaCI and their spectra were examined. In the former case above mentioned lines were hardly detected, while in the latter they appeared clearly.

Next, when a piece of metallic sodium was heated in the furnace without passing chlorine, only reversed D_{12} lines and λλ, 6161, 6154 were observed. But when chlorine gas was introduced, the above feeble lines appeared with weak intensity. Thus the presence of chlorine facilitates the emission of these lines. (Fig. 2, D, E, Pl. XIV.)

2 Potassium.

When a piece of metallic potassium was put into the heated furnace it soon burned out. In the spectrum of this light, many arc lines of potassium were obtained without accompanying enhanced lines. But when chlorine gas was introduced, potassium suddenly combined with chlorine giving a bright light. Enhanced lines λλ, 4829, 4466, 4388, etc. were detected in this light as already observed by Ramades.[1] (Fig. 2, F, G, Pl.XIV.)

These enhanced lines were clearly observed in the light emitted from the arc in chlorine, but not detected in the arc in air. (Fig. 2, H, I, Pl. XIV.)

3 Copper.

When an arc was started between copper electrodes placed in chlorine, lines at λλ, 5067, 4955, 4932, 4919, and 4910 were enhanced and at the same time lines of CuIII λλ 5381, 5369, etc. were also detected. In the spark spectrum the lines of the former group were longer than those of the latter group. (Fig. 3, O, P, Pl. XV.)

Next, an arc was started in air between the carbon and the copper electrode placed in the furnace, and the flame thus produced was examined. Only a few arc lines were detected in this light, but when chlorine was introduced, chemical combination took place suddenly and lines λλ, 5067, 4955, 4932, etc. with reversed band spectra of copper chloride were observed in the flame. (Fig. 3, L, M, Pl. XV.)

(1) Nature, **115**, 2893 (1925).

4 Magnesium.

In the furnace experiment some arc lines and the oxide band were observed in the flame. But when chlorine was introduced into the furnace, the magnesium united with the chlorine explosively giving an intense spark line λ 4481 without an accompanying oxide band. (Fig. 2, J, K, Pl. XV.) This line was also enhanced in the arc started in chlorine.

5 Zinc and Cadmium.

Spark lines of ZnII, $\lambda\lambda$ 4925, 4912 and those of CdII, $\lambda\lambda$ 5379, 5339, 4693 were enhanced in the lights emitted from the arcs in chlorine. Besides this, the following lines not observed in ordinary arcs were also detected in these lights :– ZnIII, $\lambda\lambda$ 5579, 5564, 5463, 5336, 5250, 5234, 5158, 5075, 5050, 4971, 4879, etc., and CdIII, $\lambda\lambda$ 6005, 5959, 5914, 5791, 5688, 5641, 5612, etc. In the furnace experiment the introduction of chlorine gave rise to the emission of enhanced lines of ZnII, and CdII.

6 Calcium and Barium.

As these metals could not be obtained, carbon electrodes boiled in a concentrated solution of $CaCl_2$ and of $BaCl_2$ were used as electrodes in the arc experiments, and their salts were used in the furnace experiment. The lines of BaII, $\lambda\lambda$ 4934, 4900, 4525 and those of CaII, $\lambda\lambda$ 3969, 3934 usually appearing in an air arc were found to be enhanced in the chlorine arc.

7 Mercury.

When an arc was started in air between the carbon and the mercury electrodes the line of HgIII, λ 5426 was observed only in the neighbourhood of the mercury electrode. They are not observed in the flame from the air furnace. But when chlorine was sent through the furnace this line was detected in the flame, and the lines of HgII, $\lambda\lambda$ 5679, 4959 were also observed, the former being absent in the flame when chlorine was not introduced in the furnace.

8 Aluminium.

The spark line of AlII, λ 5592 could be observed neither in the arc nor in the flame from the furnace in air, but this was detected in the arc and flame produced in the chlorine atmosphere.

9 Tin.

In the light emitted from the arc in chlorine, the lines of SnII, $\lambda\lambda$ 5800, 5590, 5563 and 5333 were enhanced as compared with those in an air arc and those of SnIII, $\lambda\lambda$ 4934, 4858, 4586, etc. were also detected. When chlorine gas was introduced into the furnace intense arc flames came out with heavy white smoke. Enhanced lines of SnII

appeared feebly in this light but not those of SnIII. (Fig. 2, A, B, Pl. XIV.)

10 Lead.

Spark lines of PbII, λλ 5609, 5545, 5273, 5043, 4387, etc. and traces of lines λλ, 5857, 4798, 4761 belonging to PbIII were detected in the light emitted from a lead arc in chlorine, but in an air arc, only lines of PbII were observed accompanied by no traces of super spark lines. In the furnace spectrum, the lines of PbII made their appearance only when chlorine gas was introduced. (Fig. 3, O, P, Pl. XV.)

11 Antimony.

In the flame obtained by heating the metal in the furnace only arc lines were observed. But when chlorine was introduced into the furnace spark lines, λλ 6080, 6005 were detected in the flame. (Fig. 3, R, S, Pl. XV.) In the arc spectrum of this metal, spark lines of SbII, λλ 6157, 6130, 6080, 6005, 5644, 5640, 5568, 5464, 5394, 5381, 5240, 5179, 5142, 5114, 4949, 4834, 4765, 4758, 4735, 4712, 4679, 4658, 4507, 4515, etc. were observed as shorter lines. By introducing the gas into the arc chamber, these lines of SbIII, λλ 6287, 6247, etc. were also observed with feeble intensities.

12 Bismuth.

In the case of bismuth it was very difficult to photograph the spectrum, for when an arc was started in chlorine gas the glass case was soon filled up with white smoke of its chloride, screening the light emitted from the arc. But the lines of BiII, λλ 5719, 5656, 5451, 5397, 5209, 5202, etc. and traces of some of BiIII could be detected in this light. The former lines appeared also in the light emitted from the furnace when chlorine was introduced.

Thus arc and furnace spectra of fourteen elements were examined in the present experiment. In the experiment with the air arc, spark lines were detected at the neighbourhood of the electrodes, but super spark lines were not observed except in a few cases. In the experiment with air only arc lines were observed without accompanying enhanced lines. But, when chlorine was introduced into the arc chamber, spark lines and some super spark lines made their appearance in the arc and in the case of the furnace spark lines were also observed. Thus the presence of chlorine in arc and furnace facilitates the emission of enhanced lines of metals in their spectra.

In conclusion, the writer wishes to express his hearty thanks to Prof. M. Kimura under whose guidance the present experiments was carried out.

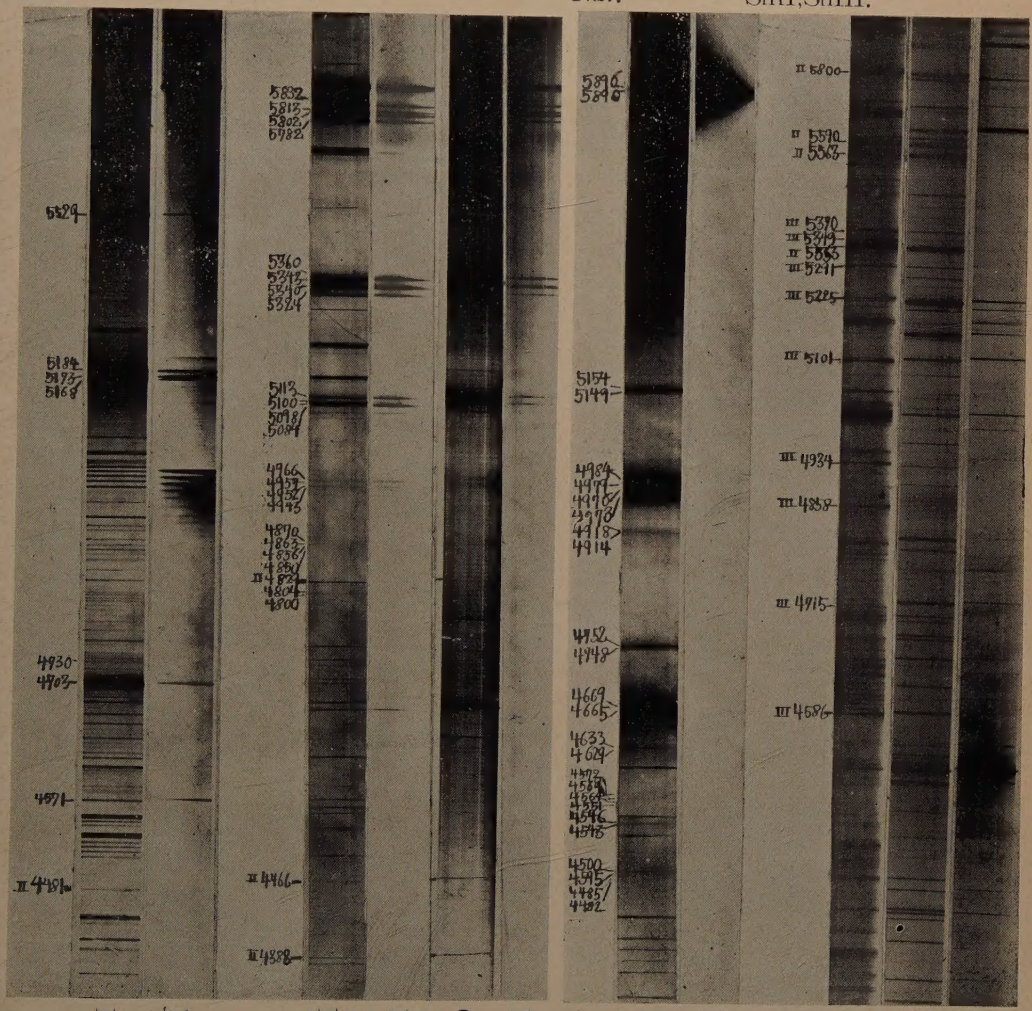

Fig. 2, Sn, Na, K, Mg Spectra.

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